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Degradation Dynamics and Persistence of Imidacloprid in a Rice Ecosystem Under West Bengal Climatic Conditions

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Rice (*Oryza sativa*) is the most important cereal crop of world. India is one of the largest producers of rice in the world. In every year, most of the yields are loses due to the attack of various insect pests like stem borer, leaf folder, brown plant hopper (BPH) and plant hoppers during the various stages of the plant growth. There are various insecticides to control these insects but most of them leave toxic residue in the different substrates of rice samples. Imidacloprid [1-(6-chloro-3-pyridimyl-methyl) – N- nitro imidazolidine-2-ylideneamine], a new generation highly active "Chloronicotinyl" group of insecticide is very effective against the various insects. Imidacloprid, first introduced by Bayer Crop Science, was very effective against resistant pests due to acting as an agonist of the nicotinyl acetylcholine receptor (Chalan and Subbratnam 1999; Olson et al. 1996; Elbert and Nauen 1996). It shows a high activity, especially against a sucking insects such as aphids, leaf and plant hoppers, thrips, whiteflies, soil insects termites and some species of chewing insects as well as seed dressing, soil treatments and foliar treatments in different crops (Jarande et al. 1994; Kumar and Santharam 1999; Kumar et al. 2001; Mote et al. 1994; Sarkar et al. 2001; Cox and Caroline 2001; Tomlin 2000). Recently it has been introduced in India and two formulations (SC &WP) are available in the Indian market. It is very effective against brown plant hopper (BPH) in rice cultivation. Very recently, M/S Excel Crop Care Ltd., Mumbai is going to introduce one new granular formulation i.e. 0.3 G in rice eco- system specially for controlling of stem borer pest complex. The present investigation was undertaken to determine the dissipation pattern as well as residue level of imidacloprid exists in soil, water, plant, grain husk and straw samples for consecutive two seasons in West Bengal climatic condition when applied @ 45 g.a.i./ha (T_1), 60 g.a.i./ha (T_2) and 90 g.a.i./ha (T_3) along with untreated control (T_4).

MATERIALS AND METHODS

A field study was conducted at University Research Farm, Bidhan Chandra Krishi Viswavidyalaya, West Bengal India for consecutive two seasons (2004 Kharif and 2005 Boro) on paddy [variety – "Khitish (IET-4094)"]. The commercial formulation of Imidacloprid (0.3 G) was applied in rice field twice at an interval

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of 15 d @ 45 g.a.i./ha (T_1), 60 g.a.i./ha (T_2) and 90 g.a.i./ha (T_3) along with untreated control (T_4). The first application was done after one month of transplanting. The insecticide was applied by broadcasting mixing with sand. Each treatment including control was replicated thrice in a randomly block designed (RBD) with plot size 5m x 4 m. The residual fate of the insecticide formulation, imidacloprid 0.3 G was studied on the three substrates i.e., field water, field soil and rice plant. For dissipation study, field water samples were collected at 0, 1, 3 and 10 d interval after first application and field soil, paddy plant samples were taken at 0, 1, 3, 10, 15, 30 and 45 d after second application. Grain, husk and straw samples were collected at harvest. All the reagents used were of analytical reagent grade and all the solvents were redistilled before use. Water used was double glass distilled.

Field water sample (500 ml) was filtered through buchner funnel using whatman No. 1 filter paper and was taken in a separatory funnel and partitioned thrice with (100 + 50 + 50) ml dichloromethane and combined organic layer was collected through anhydrous sodium sulphate. The organic layer was concentrated in a rotary vacuum evaporator at 40^0C. The concentrated extract was chromatographed over 10 g (1:1, w/w) mixture of florisil (80-120 mesh) and silica gel (60-120 mesh) in a glass column (2.5 cm ID, 65 cm length) packed with hexane with 1 cm layer of anhydrous sodium sulphate at the top. The column was eluted first with 200 ml mixture of hexane: ethyl acetate (8: 2, v/v) and the fraction was discarded. It was further eluted with 100 ml mixture of acetonitrile: methanol (9.5: 0.5, v/v). The eluate was then concentrated at rotary vacuum evaporator and reconstituted with acetonitrile for HPLC analysis.

Soil samples were collected at a depth of 0-15 cm with the help of soil auger and representative amount of sample (100 g) was kept in a conical flask with 400 ml mixture of acetonitrile: water (8: 2, v/v) for overnight. Then it was shaken vigorously for 2 h in mechanical shaker and filtered through buchner funnel using whatman No. 1 filter paper followed by washing with 150 ml of same solvent mixture. The filtrate was concentrated in a rotary vacuum evaporator at 40^0C and transferred to a separatory funnel by 100 ml distilled water. Then it was partitioned with (100 + 50 + 50 ml) dichloromethane and processed further following the same procedure as described above.

Representative samples of plant, grain and husk (25 g each) were blended with 100 ml acetonitrile in a Remi automix blender for 2 min and filtered through buchner funnel using 150 ml acetonitrile as washing solvent. Then the similar steps were followed as described above.

The field water, soil, plant, grain, husk and straw samples were analyzed by HPLC (Model No. SPD M 1O A) equipped with Diode array detector. The C-18 reverse phase column (15 cm x 4.6 mm i.d.) along with guard column was used. The mixture of acetonitrile and water (9:1, v/v) was used as mobile phase for the detection of imidacloprid residue. The other parameters like flow, wave length (9_{max}), retention time, limit of quantification (LOQ) and limit of detection (LOD)

were 1 ml, 270 nm, 2.8±0.2 min, 0.05 ppm and 0.01 ppm respectively.

In order to establish the reliability of the analytical method and to know the efficiency of extraction and clean up steps employed for the present investigation, water, soil, plant, grain and straw samples were spiked with 1, 2 and 5 ppm analytical standard of imidacloprid and the average recoveries were 82-84 %.

RESULTS AND DISCUSSION

The residue data at different day's interval, dissipation percentage, regression equation and half life values of Imidacloprid in field water, soil and plant substrates following the application @ 45 g.a.i./ha (T_1), 60 g.a.i./ha (T_2) 90 g.a.i./ha (T_3) have been presented in the table 1-6.

Table 1. Dissipation of Imidacloprid in paddy field water (1st Season).

Season	DAT	Residue in ppm [M* ± SD] (% of dissipation)		
		T_1	T_2	T_3
Kharif 2004	0	0.04 ± 0.01 (-)	0.06 ± 0.03 (-)	0.09 ± 0.07 (-)
	1	0.02 ± 0.01 (20.00)	0.04 ± 0.02 (33.33)	0.05 ± 0.04 (44.44)
	3	0.01 ± 0.01 (75.00)	0.02 ± 0.01 (66.67)	0.04 ± 0.04 (55.56)
	10	BDL	BDL	BDL
Regression equation		Y = 1.559 – 0.194X	Y = 1.771 – 0.158X	Y = 1.895 – 0.108X
Half-life (d)		1.55	1.91	2.78

Table 2. Dissipation of Imidacloprid in paddy field water (2nd Season).

Season	DAT	Residue in ppm [M* ± SD] (% of dissipation)		
		T_1	T_2	T_3
Boro 2005	0	0.06 ± 0.004 (-)	0.10 ± 0.01 (-)	0.18 ± 0.05 (-)
	1	0.04 ± 0.003 (33.33)	0.06 ± 0.01 (40.00)	0.09 ± 0.08 (50.00)
	3	0.02 ± 0.001 (66.67)	0.04 ± 0.004 (60.00)	0.06 ± 0.04 (66.67)
	10	BDL	BDL	BDL
Regressions equation		Y = 1.771 – 0.158X	Y = 1.962 – 0.126X	Y = 1.185 - 0.125X
Half-life (d)		1.91	2.39	2.41

It has been observed from the results that the residue of Imidacloprid in field water, soil and plant declined progressively with time irrespective of any dose and

season following first order Kinetics in all the doses irrespective of any season. The initial deposits of Imidacloprid after 2 h of first treatment for field water were found to be in the range of 0.04 to 0.09 ppm in kharif and 0.06 to 0.18 ppm in boro season, for soil after 2 h of second application, the initial deposits ranges from 0.29 to 0.40 ppm in kharif season and 0.28 to 0.42 ppm in boro season. In case of plant samples the initial deposits after 2 h of second application were found to be. 0.30 to 0.67 ppm in kharif season and in boro season it ranges from 1.11 to 1.83 ppm.

In case of field water, near about 75% of initial deposit is dissipated within 3 d. Half life value ranges from 1.55 – 2.78 d irrespective of treatment doses and season.

In case of soil study it is also seen that at the time of harvest no residue was detected irrespective of application rate and seasonal variation. From the present study of soil the half-life ($T_{1/2}$) values of Imidacloprid were calculated as 8.36 – 13.09 d.

Table 3. Dissipation of Imidacloprid in paddy field soil (1st Season).

Season	DAT	Residue in ppm [M* ± SD] (% of dissipation)		
		T_1	T_2	T_3
Kharif 2004	0	0.29 ± 0.09 (-)	0.38 ± 0.17 (-)	0.40 ± 0.10 (-)
	1	0.24 ± 0.08 (17.24)	0.37 ± 0.16 (2.63)	0.34 ± 0.07 (15.00)
	3	0.17 ± 0.05 (41.38)	0.20 ± 0.12 (47.37)	0.21 ± 0.09 (47.50)
	10	0.13 ± 0.04 (55.17)	0.18 ± 0.12 (52.63)	0.17 ± 0.08 (57.50)
	15	0.10 ± 0.04 (65.52)	0.13 ± 0.07 (65.79)	0.14 ± 0.10 (65.00)
	30	0.02 ± 0.02 (93.10)	0.05 ± 0.03 (86.84)	0.07 ± 0.05 (82.50)
	45	BDL	BDL	BDL
	50	BDL	BDL	BDL
Regression equation		Y = 2.435 – 0.036X	Y = 2.526 – 0.028X	Y = 2.507 – 0.023X
Half-life (d)		8.36	10.75	13.09

In case of plant samples it revealed from results that occurrence of Imidacloprid residue become maximum at 10 d after second application. After 10 d, the residue dissipated faster in the entire study. At 45 d it dissipated 87% in case of T_3 but it was not detected in T_1 and T_2 for all the seasons. The half life values were found in the range of 9.12-12.04 d. In the harvest samples no residue was detected in the

Table 4. Dissipation of Imidacloprid in paddy field soil (2nd Season).

Season	DAT	Residue in ppm [M* ± SD] (% of dissipation)		
		T_1	T_2	T_3
Boro 2005	0	0.28 ± 0.08 (-)	0.35 ± 0.11 (-)	0.42 ± 0.17 (-)
	1	0.25 ± 0.07 (10.71)	0.32 ± 0.12 (8.57)	0.34 ± 0.11 (19.05)
	3	0.19 ± 0.06 (32.14)	0.26 ± 0.07 (25.71)	0.23 ± 0.03 (45.24)
	10	0.15 ± 0.04 (46.43)	0.19 ± 0.05 (45.71)	0.16 ± 0.06 (61.90)
	15	0.12 ± 0.04 (57.14)	0.16 ± 0.05 (54.29)	0.13 ± 0.06 (69.05)
	30	0.03 ± 0.02 (89.29)	0.05 ± 0.04 (85.71)	0.07 ± 0.03 (83.33)
	45	BDL	BDL	BDL
	50	BDL	BDL	BDL
Regression equation		Y = 2.442 – 0.030X	Y = 2.539 – 0.027X	Y = 2.517 – 0.024X
Half-life (d)		10.03	11.15	12.54

Table 5. Dissipation of Imidacloprid in paddy plant sample (1st Season).

Season	DAT	Residue in ppm [M* ± SD] (% of dissipation)		
		T_1	T_2	T_3
Kharif 2004	0	0.30 ± 0.11 (-)	0.53 ± 0.16 (-)	0.67 ± 0.14 (-)
	1	0.59 ± 0.19 (-)	0.79 ± 0.33 (-)	1.09 ± 0.57 (-)
	3	0.65 ± 0.17 ()	1.08 ± 0.22 (-)	1.90 ± 0.41 (-)
	10	1.04 ± 0.39 (-)	1.72 ± 0.39 (-)	5.10 ± 1.24 (-)
	15	0.59 ± 0.37 (43.27)	1.20 ± 0.45 (30.23)	3.95 ± 0.26 (22.55)
	30	0.22 ± 0.16 (78.85)	0.44 ± 0.13 (74.42)	1.38 ± 0.13 (72.94)
	45	BDL	BDL	0.55 ± 0.32 (89.21)
	50	BDL	BDL	
Regression equation		Y = 3.307 – 0.033X	Y = 3.926 – 0.029X	Y = 3.999 – 0.028X
Half-life (d)		9.12	10.38	10.75

Table 6. Dissipation of Imidacloprid in paddy plant sample (2nd Season).

Season	DAT	Residue in ppm [M* ± SD] (% of dissipation)		
		T_1	T_2	T_3
Boro 2005	0	1.11 ± 0.09 (-)	1.18 ± 0.15 (-)	1.83 ± 0.24 (-)
	1	2.30 ± 0.18 (-)	2.99 ± 0.10 (-)	2.10 ± 0.05 (-)
	3	3.92 ± 0.14 (-)	4.05 ± 0.10 (-)	6.78 ± 0.18 (-)
	10	6.95 ± 2.57 (-)	7.21 ± 0.45 (-)	12.70 ± 0.37 (-)
	15	4.47 ± 0.27 (35.68)	3.03 ± 0.15 (57.98)	8.23 ± 0.77 (35.20)
	30	1.53 ± 0.38 (77.99)	1.85 ± 0.76 (74.34)	3.64 ± 0.71 (71.34)
	45	BDL	BDL	1.64 ± 0.97 (87.09)
	50	BDL	BDL	BDL
Regression equation		Y = 4.153 – 0.032X	Y = 4.012 – 0.026X	Y = 4.319 – 0.025X
Half-life (d)		9.41	11.58	12.04

Table 7. Harvest residues of Imidacloprid in soil, grain, husk and straw samples.

Season	Substrate	Residue in ppm (M* ± SD)		
		T_1	T_2	T_3
Kharif 2004	Soil	BDL	BDL	BDL
	Grain	BDL	BDL	BDL
	Husk	BDL	BDL	BDL
	Straw	BDL	BDL	BDL
Boro 2005	Soil	BDL	BDL	BDL
	Grain	BDL	BDL	BDL
	Husk	BDL	BDL	BDL
	Straw	BDL	BDL	BDL

BDL = Below detectable limit (<0.01 ppm)
M* = Mean of three replicate

soil, grain or straw samples. The present findings are also comparable with the earlier studies (Zhu and Xu 2000; Bhattacharyya et al. 2005). As no residue was detected in the harvest samples it might be stated that the imidacloprid may not pose any residual toxicity problems in rice production ecosystems and might be safely consumed.

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REFERENCES

Bai D, Lummis SCR, Leicht W, Beer H, Sattele BD (1991) Action of imidacloprid and a related nitromethylene on cholinergic receptors of anidentified insect motor neurone. Pestic Sci 33:197-204

Bhattacharyya A., Bhattacharyya J, Banerjee H (2005) Studies on the fate of imidacloprid – a new neonicotinoid insecticide in a rice ecosystem. The BCPC International Congress – Crop Science and Technology, 2005, 31st Oct – 2nd Nov, (2):835-840

Chalan MSV, Subbaratnam GV (1999) Insecticide resistance in cotton leafhopper, *Amrasca bugutula biguttula* (Ishida) in Andhra Pradesh, Pest Manage Econ Zool 7:105-110

Elbert A, Nauen R (1996) Bioassays for Imidacloprid for resistance monitoring against the whitefly *Bemisia tabaci*. Proceedings of Brighton Crop Protection Conference: Pest and Disease – 1996: 2:731-738

Jarande NT, Dethe MD (1994) Imidacloprid for effective control of sucking pests of chilli. Pestology 18:17-18

Kumar K, Santharam G (1999) Effect of imidacloprid against aphids and leaf hoppers on cotton. Annals of Plant Protection Science 7:212-254

Kumar R, Dikshit AK, Prasad SK (2001) Bioefficacy and residue of imidacloprid in mustard. Pestic Res J 13:213-217

Mote, VN, Datkhile RV, Pawer (1994) Imidacloprid as a seed dressing against sucking pests of Okra. Pestology 18:5-9

Mullins JW (1993) Imidacloprid : a new nitroguanidine insecticide, in pest control with enhanced environmental safety. American Chemical Society, pp. 183-198. ACS symposium Series 524: Washington DC

Olson ER., Dively GP, Nelson JO (1996) Survey of susceptibility of Imidacloprid (Admire R) in Colorado Potato beetle (Coleoptera : Chrysomelidae). Resistant Pest Manage 8:39-41

Sarkar MA, Roy S, Kole RK, Chowdhury A (2001) Persistence and metabolism of imidacloprid in different soils of West Bengal. Pest manage sci 57:598-602

Tomlin C (ed.) (2000) The pesticide Manual, 12th edn., pp. 537-538. British Crop Protection Council : Farnham UK

Zhu Y, Xu H (2000) Degradation dynamics and residues of imidacloprid in rice and soil. Acta Agriculturae Zhejiangensis 12:400-403